Semiconductor cluster beams: One and two color ionization studies of Si_x and Ge_x

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Supersonic beams of clusters of Si and Ge atoms have been produced by laser vaporization followed by supersonic expansion in a helium carrier. The cluster beams were characterized by F_2(7.9 eV) and ArF(6.4 eV) excimer laser ionization accompanied by time-of-flight mass analysis. In addition, the feasibility of a resonant two-photon ionization (R2PI) spectroscopic study was explored by two-color experiments involving initial excitation with the second (2.36 eV) and third (3.54 eV) harmonics of the Nd:YAG followed by excimer laser ionization. All two-photon ionization processes were found to produce extensive fragmentation of the larger clusters. The observed fragmentation pattern for the silicon and germanium clusters were remarkably similar to each other, but drastically different from that seen for metal clusters in the same apparatus. Unlike metal clusters, which tend to lose one atom at a time, these semiconductor clusters appear to fragment by a fission process, the daughter ions falling almost exclusively in the size range from 6 to 11 atoms. Time delay studies in the two-color experiments established that clusters of both Si and Ge have excited electronic states with lifetimes of approximately 100 ns. This again is dramatically different from the behavior found with metal clusters, and indicates the feasibility of R2PI spectroscopy on these cold semiconductor particles. The existence of such long-lived excited states indicates that there is probably an energy gap between the band of electronic states being excited and the ground electronic state.

I. INTRODUCTION

Techniques of producing cluster beams of refractory elements introduced by this laboratory[1] and others[2–4] over the past several years have produced a substantial increase in the level of research into the properties of strongly bound clusters. Using the current laser-vaporization based supersonic cluster sources it is now possible to produce rather intense cluster beams of virtually any element in the periodic table. Since the clusters are dramatically cooled in the supersonic expansion, they provide excellent subjects for detailed, high resolution spectroscopy, and a number of excellent examples of this supersonic cluster beam spectroscopy have already appeared in the literature. Primarily these have focused on small metal clusters where the key questions are concerned with the nature of the metal–metal bond, and particularly the involvement of $3d$ electrons in the bonding of such clusters as V_2,[1(e)] Cr_2,[1(b),4(c)] Cu_2,[1(c),2(a)] and Cu_3.[1(d)]

Clearly these new supersonic beam techniques are applicable to small clusters of the semiconducting elements, but as yet there have only been two papers in the area: one by Freeman *et al.*[5] in which mass-selected ions of small silicon clusters were photofragmented and a recent study of SiC_2.[6] Otherwise previous work on these clusters has been limited to studies done in cold matrices,[7] gas phase spectroscopy of dimers,[8,9] a recent study by Martin based on hot oven cluster sources and quadrupole mass spectrometry,[10] and the optical spectra of clusters in colloidal suspension.[11]

In this initial study of small clusters of silicon and germanium in a supersonic beam, we focus attention on one central question: are there any properties evident already in the small clusters of semiconductors that indicate they are different from metals? For example, is there any evidence that the bonding in small semiconductor clusters differs from that of metals? Is there any evidence of the development of a band gap in the electronic structure of the semiconductor clusters? If so, how does it develop as a function of cluster size and composition?

As detailed below, even at a fairly coarse initial level of examination there is abundant evidence that clusters of silicon and germanium are dramatically different from similarly prepared clusters of metals. In particular, it is found that the semiconductor clusters tend to fragment by a fission mechanism, rather than the simple evaporation process observed for metal clusters where fragmentation proceeds almost exclusively by the loss of single atoms. Secondly, it is found that clusters of silicon and germanium can be ionized in a sequential two-photon process where the first photon prepares an excited state that lives on the order of 100 ns. The presence of these relatively long-lived excited states is quite a departure from the behavior of small metal clusters where extremely rapid radiationless transitions amongst a high density of vibronic states is the rule. We interpret the presence of metastable excited states as evidence for the development of a band gap which prevents electronic excitation from being completely converted into vibrational heating on a subnanosecond time scale as is the case with metal clusters.

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II. EXPERIMENTAL

A detailed description of the apparatus used in this study has been given previously.[1] In brief, a 0.63 cm diameter rod of the semiconductor was placed in the throat of a pulsed supersonic nozzle. The second harmonic (40 mJ/pulse) of a Nd:YAG laser was focused onto a 0.1 cm spot on the rod, and fired approximately 30 μs before the time of maximum He carrier gas density over the rod ($\sim$1–2 atm). The plasma/helium mixture flowed through a 0.2 cm diameter by 1 cm long channel into a cluster formation/thermalization zone (discussed below). Free expansion of this cluster/helium mixture into a large vacuum chamber then produced an intense supersonic jet which was collimated by a skimmer 30 cm downstream from the nozzle. Previous experience with this apparatus for a wide variety of metal clusters indicates that these conditions produce extreme cooling of all internal degrees of freedom in the clusters.

After passing through two stages of differential pumping, the supersonic semiconductor cluster beam then entered the ionization region of a time-of-flight mass spectrometer (TOFMS). One-color ionizations were done either with an excimer laser fired perpendicular to the molecular beam or with the third harmonic of a Nd:YAG laser fired down the beam axis. Two-color ionizations and excited state lifetime studies were performed by firing the YAG laser down axis and then firing the excimer laser cross axis after a programmed delay. Following ionization, the cluster photoions were accelerated down a 1.5 m long TOF drift tube and detected by an electron multiplier.

The main timing sequence was controlled by an IBM-XT microcomputer interfaced to a microsecond delay generator through a camac crate. The experiment repeated at a rate of 9 Hz, and most experiments were run for at least a thousand cycles in order to average instrumental fluctuations. A nanosecond delay generator was used to perform the excited state lifetime scans. The delay between the two ionizing lasers could be varied in increments of 10 ns from 0 to 600 μs.

A. The cluster formation/thermalization zone

One of the most critical parameters within a laser vaporization cluster source is the channel which connects the cluster source to the supersonic expansion. Within this channel the laser-induced plasma must recombine, hot atoms must thermalize, combine to form clusters, and the binding energy released in the cluster formation must be dissipated in collisions with the helium carrier gas. Over the short times involved, only a very small portion of the excess energy of the vaporization pulse can be transferred to the nozzle walls; most remain as heat in the helium carrier gas.

Because of the importance of this region, this group has done extensive designing and testing of different exit channel geometries. One of the most effective designs has proved to involve an extended cluster formation/thermalization zone consisting of a 1.5 cm long, 0.4 cm diam tube with a 0.25 cm diam (sonic) exit orfice (see Fig. 1). This short extra zone is mounted on the end of the standard pulsed nozzle, and provides a number of benefits. First, the zone serves to mix the short region of the helium flow containing the hot plasma

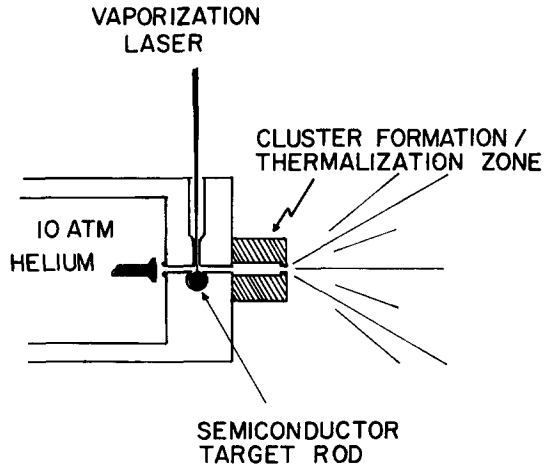

FIG. 1. Schematic cross section of pulsed semiconductor cluster nozzle used in this research. Semiconductor vaporization is done by a 50 ns long, 30 mJ pulse of green light from a frequency doubled Nd:YAG laser. The ejected semiconductor plasma is entrained in helium flowing at near sonic velocity in a 0.2 cm diam, 1.0 cm long channel which terminates in the cluster formation/thermalization zone (crosshatched area). This zone is a 0.4 cm diam, 1.5 cm long channel with a 0.25 cm diam exit orifice. The geometry of this zone enhances the clustering process and spreads the clusters out over a 100 μs long pulse.

with cool helium from regions of the flow immediately preceeding and succeeding the vaporization laser shot, thus producing a lower overall buffer gas temperature. Second, the 100 μs mean residence time in this added zone (adjustable by varying the exit orifice diameter) provides sufficient time for extensive clustering to occur, and adequate time for collisions with the helium buffer gas ($\sim$1 atm) to bring the internal temperatures of the clusters to near room temperature. Third, and perhaps most important, this added zone spreads out the portion of the helium pulse containing the clusters to 100 μs, effectively eliminating pulse-to-pulse intensity fluctuations due to small changes in the supersonic beam velocity.

III. RESULTS AND DISCUSSION

A. ArF laser photoionization–Evidence for cluster fission

One of the most remarkable and significant observations of this study was made in its very first few days when the TOF mass spectra of silicon and germanium cluster beams were recorded using the 6.4 eV output of an ArF excimer laser for ionization. As shown in Fig. 2, silicon and germanium cluster beams produce almost identical mass spectra under these conditions. At the moderate excimer laser fluence used (roughly 0.5 mJ/cm^2), both semiconductor beams show very intense ion production in the mass range up to and including clusters with 11 atoms, with very little cluster ion signal being seen for higher clusters. The cluster ion signal in the size range between 6 and 11 atoms is particularly strong for both these semiconductor elements.

Careful examination of the peaks in the figure shows that these cluster ion peaks in the 6 to 11 range are different from those in the 1–5 range: the higher-range cluster signals all show a distinct tailing of intensity toward the high mass

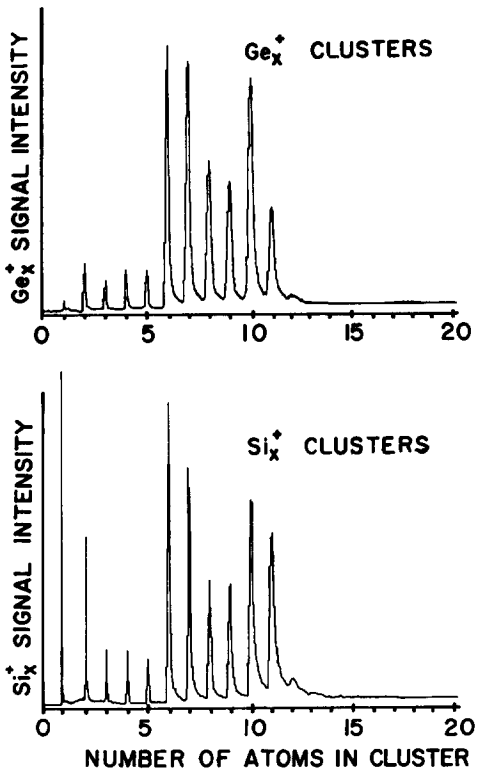

FIG. 2. Time-of-flight mass spectrum of germanium and silicon clusters. The clusters were ionized with a moderate fluence (0.5 mJ/cm^2) ArF excimer (6.4 eV). All cluster peaks shown are results of multiphoton ionizations. The right-handed tails on the peaks for clusters containing 6–11 atoms indicate that fragmentation from higher masses contributes to these channels. The instrument is optimized to observe clusters in the size range 6–20.

side. In a TOF mass spectrum this asymmetry indicates that the ions are fragmenting in the extraction region of the ion source, and the observed ions are actually fragmentation daughters of higher clusters. The observed fact that both the silicon and germanium cluster beams display such a remarkably similar TOF mass spectrum under these conditions leads us to two key conclusions:

(1) The nascent cluster size distribution in the supersonic beam must be essentially the same for both silicon and germanium, and

(2) The fragmentation behavior of these clusters under ArF irradiation is also essentially the same for Si_x and Ge_x. Cluster ions of both elements fragment primarily into daughter ions in the 6–11 atom size range.

We are discounting here the only other possible explanation which is that the nascent cluster distributions in the beam are markedly different for silicon and germanium, but the ArF laser fragmentation behavior differs between the two elements in just the way required to make the observed ionization TOF mass spectra appear the same. We know of no reason to expect such an exact compensation of beam density variations by detectivity variations.

Not only is this ionization/fragmentation behavior remarkably similar for silicon and germanium clusters, but it is dramatically different from any photofragmentation behavior we have ever observed on this apparatus. Although these are the first semiconductor elements we have studied in detail, there is an extensive tradition of experiments with metal clusters on this same machine.[1] At the time of this writing, cluster beams of 15 different metallic elements have been studied in this fashion, and not one has displayed a photofragmentation behavior even remotely similar to that seen in Fig. 2.

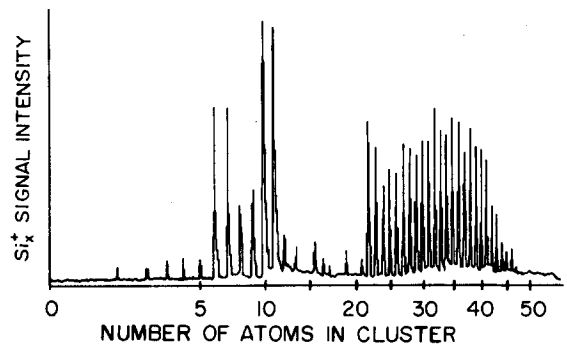

FIG. 3. Mass spectrum of silicon clusters ionized with a low fluence (0.05 mJ/cm^2) ArF excimer (6.4 eV). The instrument is optimized to observe clusters in the size range 6–20. Note the onset of one-photon ionization at Si_{22}.

Ordinarily, we expect to observe a very extended cluster distribution when ionizing with moderate ArF excimer laser fluence—Fig. 3 of Ref. 1(c) shows some very typical examples for a variety of metals. In these metal cluster beams the effect of higher ArF excimer laser fluence is simply to shift the observed cluster distribution down smoothly to emphasize the smaller clusters. In a new cluster ion photodissociation apparatus we have recently demonstrated[12] quite clearly for a variety of metal cluster ions that the dominant primary fragmentation process of a metal cluster is the loss of a single metal atom. Metal cluster ions simply evaporate,

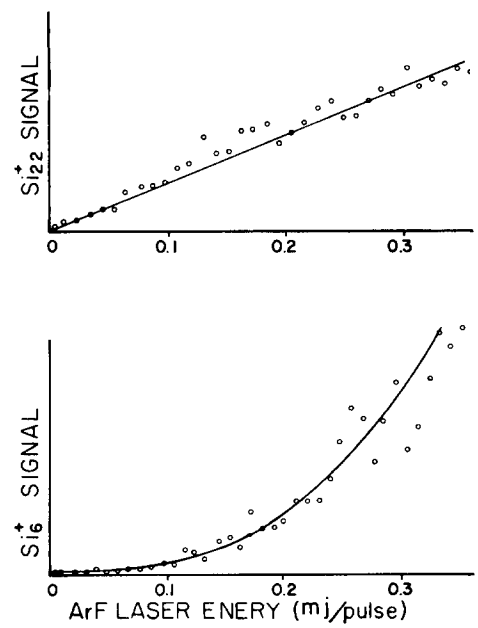

FIG. 4. Dependence of Si_{22}^+ and Si_6^+ signals on ArF excimer laser photon fluence. The linear dependence of the Si_{22}^+ signal indicates a one-photon ionization process, whereas the quadratic dependence of the Si_6^+ signal indicates a two-photon ionization process.

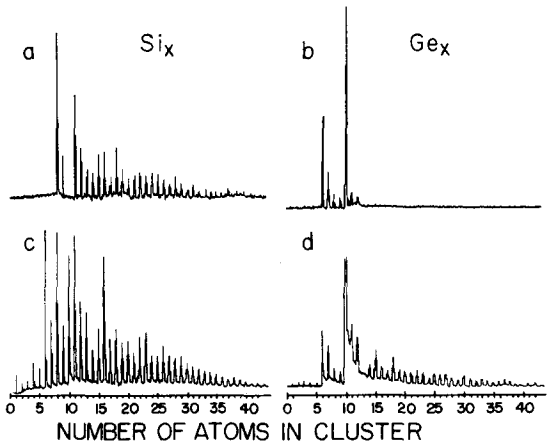

FIG. 5. Time-of-flight mass spectra of clusters ionized by a F_2 excimer laser at 0.01 mJ/cm^2 (top) and at 0.2 mJ/cm^{-2} (bottom) for both silicon and germanium supersonic cluster beams.

giving off one atom at a time. Figure 2, on the other hand, shows this is definitely not the case for semiconductor clusters. Both Si_x and Ge_x show a marked tendency to fragment by *fission* to give daughter ions almost exclusively in the 6–11 atom size range.

Figure 3 makes this point about fragmentation by fission even more clearly. Here the TOF mass spectrum of Si_x clusters is shown for extremely low ArF excimer laser fluence (0.05 mJ/cm^2). At this low photoionization laser fluence the higher silicon cluster ions are less likely to absorb a second photon and fragment, so many appear in the mass spectrum at their correct mass. Generally, one expects that the ionization potential of a cluster will decrease with increasing cluster size. As seen in the figure, the first silicon cluster with an ionization potential lower than the 6.4 eV ArF excimer laser photon is apparently Si_{22}. The fact that this is a direct one-photon ionization process is established by the data of Fig. 4(a) which shows a linear dependence of the Si_{22} photoion signal on ArF laser fluence. Similarly, the photoionization signals for all clusters higher than Si_{22} were also found to be one-photon, direct ionization events.

The cluster ion signals in the 6–11 atom range of Fig. 3, however, turned out to be two-photon ionization events. This is clearly shown in Fig. 4(b) which displays the Si_6 photoion signal intensity as a function of ArF excimer laser fluence.

Perhaps the most remarkable aspect of Fig. 3 is the absence of any strong ionization signal in the cluster size range between 12 and 22 atoms. This is one of the cleanest evidences for fragmentation by fission. The asymmetry of the peaks in the 6–11 size region indicates they are fragments, not parent ions. The absence of strong ion signals in the 1–5 and 12–21 size range indicates that for the distribution of cluster sizes produced by this cluster source, fragmentation is almost uniquely into clusters in the 6–11 atom range.

B. F_2 laser photoionization

Ordinarily, based on our experience with metal cluster beams we expect photoionization with the F_2 excimer laser at 7.89 eV to give a fairly accurate, unbiased TOF mass spectrum which shows the nascent cluster distribution in the beam. For these semiconductor clusters, however, F_2 laser photoionization has proved to be less readily interpretable. Figure 5 displays the observed cluster photoion TOF mass spectrum for both silicon and germanium clusters at two fluences of the F_2 laser. The ionization patterns for silicon are roughly what we would expect. With the exception of Si_7 and Si_8, the first silicon cluster that is directly photoionized by the 7.89 eV photon of the F_2 laser is Si_{11} [Fig. 5(a)]. Above Si_{11}, the F_2 laser reveals that all clusters are represented in the beam with roughly monotonically decreasing density as a function of cluster size. At higher laser fluences [Fig. 5(c)], absorption of further laser photons causes fragmentation of higher clusters down to the 6–11 size range, and allows the smaller clusters in the 1–5 atom range to be observed in a two-photon ionization process.

Germanium, however, displays a markedly different ionization behavior. At low F_2 laser fluence [Fig. 5(b)], Ge_6 and Ge_{10} are by far the most intense cluster ions observed, with essentially nothing detectable above Ge_{12}. At higher laser fluence [Fig. 5(d)], a bit of signal is seen for the larger clusters, but Ge_{10} in particular has grown until it truly dominates the observed TOF mass spectrum. Since the ArF ionization patterns are so similar, we believe the nascent cluster distributions in the germanium and silicon cluster beams must be essentially the same. This drastic difference in the F_2 laser ionization behavior must therefore be a result of marked variations in the photoionization cross sections at 7.89 eV for these germanium clusters. In the current absence of other readily available ionization lasers in this wavelength region, it will be difficult to obtain any further understanding of this effect. Regardless of the details of the ultimate explaination, it is clear from these data that Ge_{10} is a very unusual cluster indeed.

C. Two-color photoionizations–Evidence for long-lived states

The facile two-photon ionization (R2PI) of moderately large clusters by the ArF excimer laser discussed above in Sec. III A suggested that these semiconductor clusters may differ from metal clusters in more that just their fragmentation behavior. Our experience thus far with a wide range of metal clusters is that efficient R2PI is highly exceptional for clusters with more that two atoms. In fact, at this writing, successful R2PI spectroscopic studies have been reported for only one transition metal trimer (Cu_3).[1(d)] In even small metal clusters the density of excited electronic states is extremely high even within the first 1–2 eV of the ground state. Generally the coupling between these electronic states is quite strong and any excitation produced in one particular excited state by interaction with a laser is very rapidly dissipated into vibrational excitation in the low-lying electronic states of the cluster. Subsequent absorption of a second photon from the laser does not result in ionization since the original electronic excitation of the first photon has been divided amongst the large number of vibronic degrees of freedom of the cluster.

Semiconductor clusters, however, might be expected to behave quite differently from metals since even in the macro-

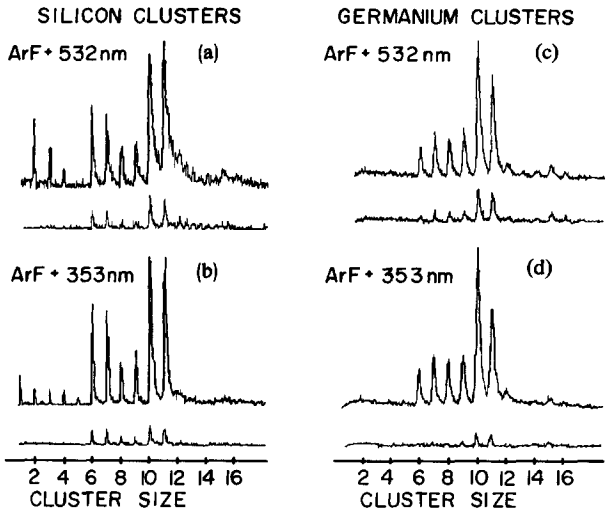

FIG. 6. TOF mass spectra of two-color ionized silicon and germanium clusters. The Nd:YAG laser pulse precedes the ArF excimer pulse by 10 ns, and the instrument is optimized for clusters of 6–21 silicon atoms (6–15 germanium atoms). The baseline spectra were taken with the Nd:YAG laser blocked. Laser fluences used to obtain these data (in mJ/cm^{-2}): (a) second harmonic = 35, ArF excimer = 0.02; (b) third harmonic = 10, ArF = 0.02; (c) second harmonic = 30, ArF = 0.02; (d) third harmonic = 10, ArF = 0.01.

scopic, bulk form long-lived electronic excitations are often found either in the conduction band or as trap levels within the band gap. A variety of theoretical calculations of semiconductor cluster electronic structure have appeared in the recent literature,[13–21] most of which reveal a substantial gap between the ground electronic state and the excited electronic states—a gap which is increasingly well defined as the cluster size increases. One of the central tenets of radiationless transition theory is that large gaps between electronic states reduce the rate of electronic energy decay. Measures of the relaxation dynamics of the excited electronic states of semiconductor clusters may therefore be expected to offer us a first indication of the evolution of this bulk band structure.

Figure 6 shows the results of a series of two-color R2PI experiments on the silicon and germanium cluster beams. For these experiments one of the harmonics of a Nd:YAG laser was directed down the axis of the supersonic beam and triggered such that it irradiated the clusters in the beam just 10 ns before they were hit by the ArF excimer laser in the ionization region of the TOF mass spectrometer. When the 1.06 μ (1.2 eV) fundamental of the Nd:YAG was used, no effect could be detected, even at fluences up to 100 mJ/cm^2. However, as shown in Fig. 6, both the second and third harmonics of the Nd:YAG laser produced strong enhancements of the ionization signal. These enhancements were observed only when the ArF laser was on as well—they are true two-color R2PI signals. Once again, the same pattern is observed in the mass spectrum for the two semiconductors. Primarily it is only the clusters in the 6–11 range that are seen, and there is a clear asymmetry to the peaks indicating a significant contribution of photofragment daughters from larger clusters.

By varying the time delay between the two lasers, it was possible to measure the evolution of the excited state produced by the YAG harmonics. Figure 7 shows a few typical decay curves observed for this two-color R2PI excitation as observed in the Si_{10}^+ and Ge_{10}^+ photoion mass channels. Similar two-color ionization behavior was observed in all cluster signals in the 6–11 range (see Table I), but the behavior of the photoion signal appearing in the Ge_{10}^+ channel was studied with particular care.

As discussed in Sec. III A, the ArF laser alone is capable of producing strong photoionization signals in the Ge_{10}^+ channel. As in the case of Si_6^+ as shown in Fig. 4, this "ArF only" ionization exhibits a quadratic laser power dependence. However, when the YAG second or third harmonic laser excites the cluster beam 10 ns before the ArF laser, the

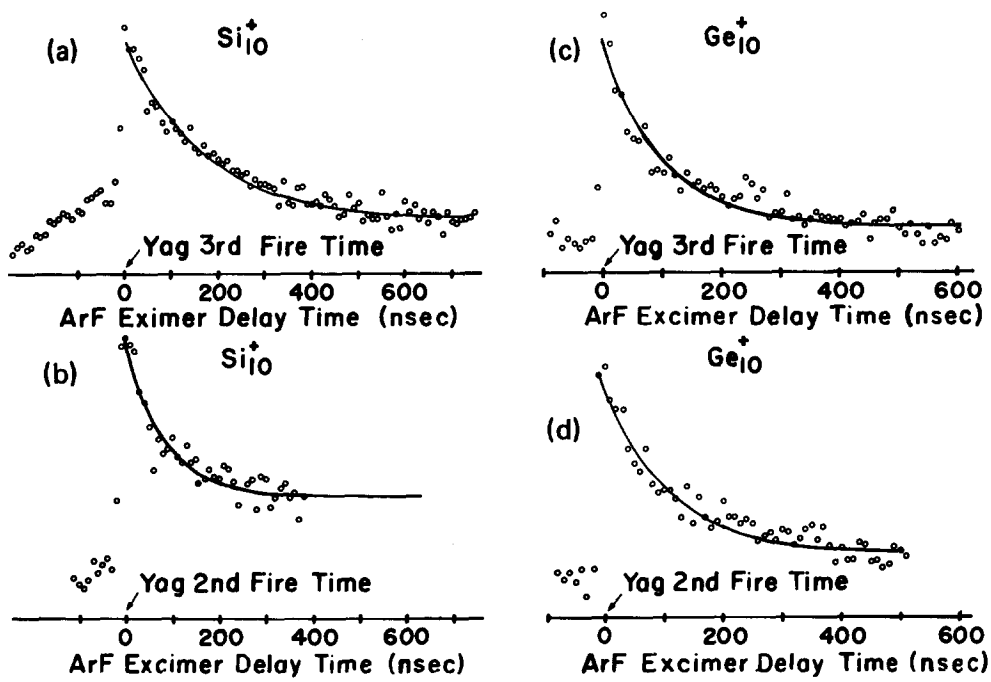

FIG. 7. Time dependence of the two-color ionization signal in the Si_{10} and Ge_{10}^+ channel for the case of YAG third harmonic excitation (top) and second harmonic excitation (bottom). The horizontal axis is the time delay between the YAG excitation laser used to produce excited states of the clusters and the ArF excimer laser used to ionize these excited states. Laser fluences used to obtain these data were (in units of mJ/cm^{-2}): (a) third harmonic = 30, ArF = 0.02; (b) second harmonic = 45, ArF = 0.01; (c) third harmonic = 10, ArF = 0.01; (d) second harmonic = 30, ArF = 0.01.

TABLE I. Lifetimes of the excited states associated with 6–11 cluster ions of silicon and germanium excited by various harmonics of a Nd:YAG laser. The columns labeled "530 nm" correspond to excited states produced by the second harmonic, those labeled "353 nm" by the third. Lifetimes are in nanoseconds and represent the best fit of the data to a single exponential decay. Stated errors are estimated 95% confidence limits.

	Silicon		Germanium	
	530 nm	353 nm	530 nm	353 nm
6	...	144 + 2	72 + 19	74 + 11
7	...	166 + 3	85 + 24	69 + 7
10	96 + 19	173 + 2	116 + 26	110 + 5
11	82 + 18	294 + 7	119 + 29	106 + 11

signal becomes linearly dependent on ArF fluence. Figure 8(a) shows this for the case of two-color ionization to produce Ge_{10}^+. Both the second and third harmonic of the YAG laser are capable of producing excited states which are one-photon ionized by the ArF excimer laser. In the case of the YAG third harmonic, this intermediate state is excited in one-photon process, as shown by the linear laser power dependence of Fig. 8(c). For the second harmonic, the power dependence shown in Fig. 8(b) reveals the relevant excited state is produced in a two-photon process.

Careful examination of the decay curves of Fig. 7 reveals there are a few other effects of the YAG laser excitation in addition to the production of excited states that can be one-photon ionized by the ArF excimer laser. Particularly in the decay curve shown for Si_{10}^+ under third harmonic excitation [Fig. 7(a)], it is clear that there is some ionization signal produced even when the ArF laser fires *before* the YAG laser. Upon subsequent careful experiments this turned out to be due to a rather efficient multiphoton ionization process involving the YAG third harmonic alone. The apparent time dependence of this signal is an artifact resulting from strobing the ion signal across the TOF channel as the YAG pulse is moved with respect to the ArF (which determines the TOF timing). Similarly intense multiphoton ionization signals were observed for germanium clusters as well at third harmonic fluences of greater than 20 mJ cm^{-2}.

A second auxiliary effect of YAG laser excitation is that some of the larger clusters absorb enough photons to fragment as they travel down the supersonic beam. This produces an increased concentration in the beam for the smaller clusters, which in turn raises the base line signal seen in Fig. 7 due to two-photon ionization by the ArF excimer laser. This fragmentation enhancement effect is particularly evident in the decay curve corresponding to second harmonic excitation of the silicon clusters [Fig. 7(b)]. For sufficiently long delays after the YAG laser excitation, these fragments will drift out of the supersonic beam due to the excess energy released in the fragmentation process, and such effects have been seen with this apparatus on a 10–100 μs time scale. The relatively fast (100 ns) decays shown in Fig. 7, however, cannot possibly arise from such a fragmentation mechanism. In order for fragments this massive to leave the 1 cm diam supersonic beam in 100 ns, over 1000 eV excess energy would be necessary in the translational degrees of freedom.

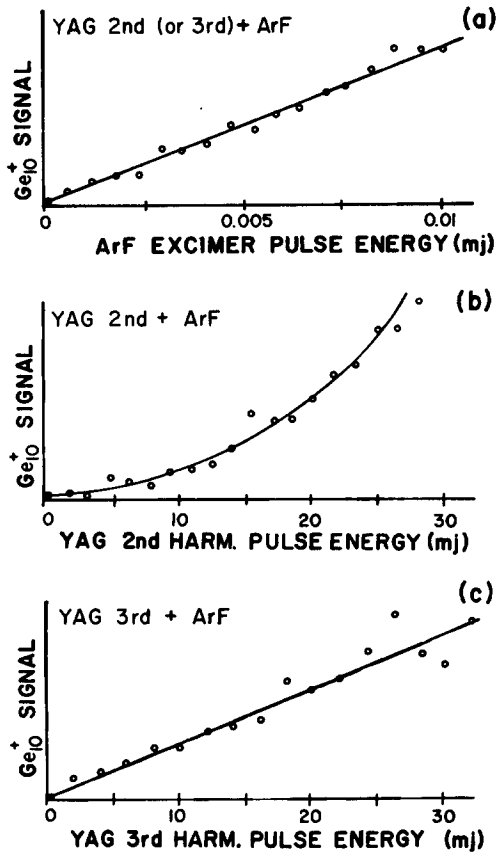

FIG. 8. Power dependence of the two-color ionization signal in the Ge_{10}^+ channel. All data taken with YAG laser pulse preceding ArF excimer laser pulse by 10 ns. (a) Linear dependence of ion signal on ArF excimer power for YAG second harmonic (30 mJ/cm^{-2}) [or third harmonic (10 mJ/cm^{-2})] excitation. (b) Second quadratic dependence of ion signal on YAG second harmonic power with ArF laser power constant at 0.01 mJ/cm^{-2}. (c) Linear dependence of ion signal on YAG third harmonic power with ArF laser power constant at 0.01 mJ/cm^{-2}.

IV. SUMMARY AND CONCLUSIONS

In this first exploratory study of the properties of small clusters of silicon and germanium we were most interested in what differences, if any, would distinguish clusters of semiconducting elements from those of metals. In fact, even with the simple tools of crude mass analysis of the ions produced with a few fixed freqency lasers, the differences turn out to be striking in virtually every respect.

First, there is the difference in fragmentation mechanism. Germanium and silicon clusters are amazingly similar in their tendency to fragment to small units containing 6 through 11 atoms—units which must be particularly stable configurations. As this work was in progress, results of a similar study by Freeman *et al.* were announced[5] where mass-selected ions of small silicon clusters were photofragmented. There is rough agreement between our study and theirs: they also find that fragments in the 6–11 range are by far the most favored. A similar mass-selected cluster ion photofragmentation apparatus in our laboratory[10] has performed a wide variety of laser dissociation studies on metal clusters such as Fe_x, Ni_x, and Nb_x. The results from these metallic systems are dramatically different: all these metal clusters fragment simply by throwing off a single atom, i.e., just like the bulk metal, they evaporate to form a primarily

monatomic vapor. So this observation that silicon and germanium clusters tend to fragment by a fission mechanism to produce clusters in the 6–11 range is quite striking indeed.

Second, there is the difference in excited states dynamics. With the exception of one low-lying state of Cu_3, there are no excited electronic states known for any metal cluster with more than two atoms which lives longer than 1 ns. Although it is likely a few more isolated band systems in a few special metal clusters will be found, extensive searches have been carried out in this laboratory over the past several years using highly sensitive R2PI techniques for a broad range of metal clusters, and (with the possible exception of silver), no other long-lived excited states have been found. In other words, metal clusters even with three atoms have the radiationless properties of metals: there is an extremely high density of low-lying electronic states very efficiently coupled by vibrations (phonons).

The time-delayed two-color laser ionization studies reported here are the first such studies performed on silicon and germanium clusters. They show that these clusters are drastically different from any metal clusters ever studied by these techniques. In the same sense that metal clusters display the radiationless properties of metals, these semiconductor clusters are displaying the radiationless properties of semiconductors: long-lived excited states associated with the band gap.

Without detailed wavelength-dependent R2PI scans, it is impossible to say much yet about the excited electronic state manifolds of these clusters. However, it should be possible to carry out such R2PI studies, and they would probably be quite worthwhile. There is the problem of facile fragmentation into the 6–11 cluster range, which in some cases will make it difficult to decipher the spectrum of one neutral cluster from another. But there are depletion-detected spectroscopies available to help in the sorting out,[1(d)] and experiments along these lines are currently being pursued in this laboratory.

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